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**INFRARED SPECTROGRAPHIC ANALYSIS OF SOME
PRESERVATIVE, HYDRAULIC, AND SPECIALTY FLUIDS**



TECHNICAL REPORT

By

Bernard J. Bornong

February 1967

**U. S. ARMY WEAPONS COMMAND
ROCK ISLAND ARSENAL
RESEARCH & ENGINEERING DIVISION**

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INFRARED SPECTROGRAPHIC ANALYSIS OF SOME PRESERVATIVE,
HYDRAULIC AND SPECIALTY FLUIDS

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ABSTRACT

An effort was made to ascertain whether infrared spectrographic analysis could detect changes in composition of formulations of preservative, hydraulic and specialty fluids covered by specifications for which Rock Island Arsenal has qualification responsibility. Limits of detection of additives were estimated using both spectra compensated by base oil in the reference beam of the spectrophotometer and simple, or uncompensated spectra. Petroleum type base oils for VV-L-800 and MIL-H-46004 and a tetra-alkyl silicate base fluid for MIL-L-14107 were used. Additives studied were several corrosion inhibitors, antioxidants, antiwear agent, a hydrolysis inhibitor, a pour point depressant and a dye. It was found that the heavy absorption of the silicate base oil obscured absorption bands of all additives tested in it. In the petroleum base oils the corrosion inhibitors and tricresyl phosphate were easily detected. The remaining additives are used near or below their detection limits. Use of the formulation's base oil in the reference beam improved the limit of detection of additives. It was concluded that the infrared spectrogram cannot accurately detect changes in formulation. The recommendation is made that methods for concentration of additives be used before obtaining the infrared spectrogram in order to improve on their detection.

FOREWORD

This work unit was initiated in FY65 under the title "Use of Infrared Spectrographic Analysis for Identification of Specific Formulations." It was continued in FY66 under the title "Infrared Spectrographic Identification of Corrosion Preventive and Preservative Oil Formulations" under DA Project Number 1CO24401A109. It is intended to use information gained in this work to improve inspection methods for corrosion preventive, hydraulic and specialty fluids purchased by the Army and other government agencies. The work is part of the Rock Island Arsenal Laboratory's research and development effort on Corrosion Preventive and Specialty Compounds. Infrared spectrograms for this report and some interpretations of spectra were furnished by Mr. L. H. Moorhead and Mr. O. J. Littig of the Laboratory's Analytical Unit.

TABLE OF CONTENTS

	<u>Page No.</u>
Title Page	1
Abstract	2
Foreword	3
Table of Contents	4
Problem	5
Background	5
Approach	6
Results and Discussion	8
Conclusions and Recommendations	21
Distribution	22
DD Form 1473 (Document Control Data - R&D)	26

PROBLEM

Military specifications describe formulations for corrosion preventives, hydraulic fluids and specialty compounds in terms of performance and other data on a finished product. Qualification tests are performed on products submitted by manufacturers to determine whether they meet the requirements of the applicable specification. Once a product has been qualified and subsequently purchased, it may be subjected to further testing to see that it continues to conform to the specification. In some cases, it may be possible for a manufacturer to substitute inferior materials, or otherwise change the formulation, and claim that the product is the same as that which was qualified. Present test methods are not always capable of detecting such changes. A simple, rapid method of detecting changes in formulation is needed.

BACKGROUND

The infrared spectrum covers wavelengths of electromagnetic radiation from approximately 0.75 microns to 1 mm. Of greatest practical interest to the chemist is the region between wavelengths 2 and 16 microns, or frequencies expressed in wavenumbers between 5000 and 625 cm^{-1} . Radiation in this region is absorbed by organic molecules and converted into energy of molecular vibration. The energy absorption pattern obtained is referred to as the infrared spectrum. In its usual form, the spectrum is a plot of intensities, as percent transmittance or absorbance of energy, versus wavelength, in microns, or frequency, in cm^{-1} , of absorption.

Interpretation of spectra are done chiefly on an empirical basis. Even a fairly simple molecule can give a complex spectrum. To deduce molecular structures directly from complex spectra would be a difficult task although for some problems this has been done. The complexity of the spectrum is an advantage, in that the spectrum of an unknown compound can be matched with the spectrum of a known sample. A peak-by-peak correlation is evidence of identity. Certain groups of atoms, on the other hand, are characterized by absorption at or near certain group frequencies regardless of the structure of the rest of the molecule. These characteristic group frequencies are also useful in identification work.

Infrared analysis is a tool for quantitative as well as qualitative analysis. The intensity of absorption is related to the quantity of absorbing species present in the sample. The relative positions of the absorption peaks are not changed, or only slightly changed, by changes

in concentration.

The complexity of the spectrum of even simple molecules brings difficulties into the use of infrared spectroscopy for analysis of mixtures. Here again, however, a point-by-point correlation should give evidence of identity or non-identity of formulations. Infrared analysis has been applied, apparently with some success, to petrolatum corrosion preventives^(1,2), specification MIL-L-21260 lubricants⁽³⁾ and sulfonate additives⁽⁴⁾. Crilly's work⁽³⁾ indicates that, in the spectra of two oil samples, differences in transmittance as small as $\pm 2\%$ in the regions between 5.5-6.5 microns, or 1820-1540 cm^{-1} , and 8-13 microns, or 1250-770 cm^{-1} , is sufficient to indicate that two oil samples are different. These wavelength or frequency limits apply to formulations in base oils derived from petroleum, but not necessarily to other types of base oil.

APPROACH

The initial approach was to obtain qualification and surveillance samples covered by thirteen specifications for which Rock Island Arsenal has qualification responsibility. As a file of spectra was built up, the spectra of qualification and surveillance samples were to be compared and correlated with laboratory reports covering the same samples. However, because of the relatively slow accumulation of samples, it soon became apparent that it would require a long time before any meaningful

1. Freeman, R. R. and Wagner, L. H., "Infrared Absorption Spectra of Petrolatum Type Corrosion Preservatives," Rock Island Arsenal Laboratory Report 56-1175, 27 April 1956.
2. Wagner, L. H., "Storage Stability of Petrolatum Type Corrosion Preventive Compounds," Rock Island Arsenal Laboratory Report 60-1366, 28 April 1960.
3. Crilly, J. B., "Acceptance Test for Preservative Lubricants Based on Infrared Spectra," U. S. Naval Civil Engineering Laboratory Technical Report 098, Port Hueneme, California, 13 December 1960.
4. Crilly, J. B. and McGowan, R. J., "Infrared Measurement of Sulfonate Additives," U. S. Naval Civil Engineering Laboratory Report R190, Port Hueneme, California, 11 April 1962.

correlation could be made between spectra and laboratory tests.

The approach was then modified. Mixtures of some known ingredients commonly used in formulations were made up and their spectra obtained. If one or more of these ingredients escaped detection when added to a base oil, this would be sufficient to show that the infrared spectrogram, by itself, could not satisfy the objectives of this program. This report summarizes results obtained on complete and partial formulations of materials under specifications MIL-C-372, VV-L-800, MIL-L-3150, MIL-L-14107 and MIL-H-46004.

Materials used were as follows:

1. Base oils.

VV-L-800 base oil. Refined petroleum fraction.

MIL-L-14107 base oil. Tetra-(2-ethylhexyl) ortho silicate.

MIL-H-46004 base oil. Refined petroleum fraction.

2. Additives.

(a) Corrosion inhibitors or surfactants.

Calcium petroleum sulfonate, 35% active soap. Vehicle not specified.

Barium dinonylnaphthalene sulfonate 50% dispersion in coastal extracted mineral oil.
Nonylphenoxycetic acid, 90%.

Oleoyl-linoleoyl sacrosine. 94% min.

(b) Antioxidants.

Cadmium diamyl dithiocarbamate. 50% in solvent refined coastal oil.

Phenyl-alpha-naphthylamine. C. P.

2,6-di-tert-butyl-p-cresol. 98.5%.

p,p'-Diocetyldiphenylamine. Purified.

(c) Anti-wear agent.

Tricresyl phosphate (TCP), technical grade.
80% para. 20% meta.

(d) Pour point depressant.

Poly acrylate. Mol. wt. not specified.

(e) Color.

"Oil Yellow N." duPont

(f) Hydrolysis inhibitor.

Quinazarin. Technical grade.

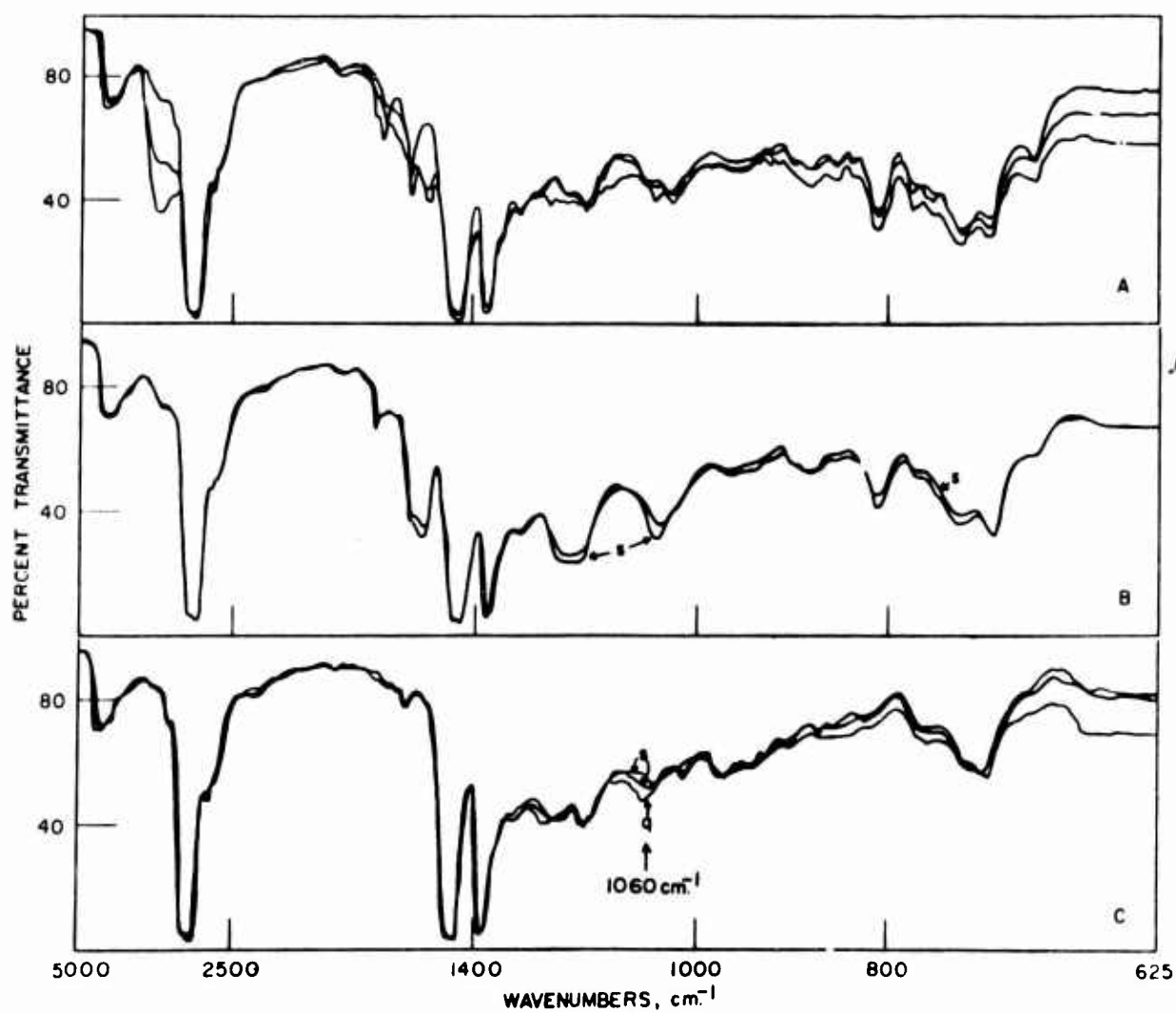
Infrared spectra were obtained on a Baird Atomic, Inc. Double Beam Infrared Recording Spectrophotometer which has been described in a Rock Island Arsenal technical report⁽¹⁾. Most spectra on base oils and formulations were obtained in cells using 0.10 mm. lead spacers between salt windows, with only NaCl in the reference beam. Some spectra were obtained using 0.025 mm. Teflon spacers. Other spectra of formulations were obtained with samples of the base oil in a variable path length cell placed in the reference beam of the spectrophotometer. Spectra of additives were obtained either in a KBr pellet or by the capillary method, i.e., between salt windows with no spacer used. All spectra were measured in the region 5000-625 cm^{-1} wavenumbers, or 2-16 micron wavelength.

RESULTS AND DISCUSSION

Figure 1 shows infrared absorption spectra of several finished preservative formulations furnished by three manufacturers. In Figure 1A the superimposed curves show considerable variation between a qualification and two surveillance samples of MIL-C-372 bore cleaner. All three samples met laboratory test requirements of the specification. No separate identification of the three curves in Figure 1A is made because they cross at numerous points.

Figure 1B shows superimposed spectra of two MIL-L-3150 preservative lubricants. One is a qualification and the other a surveillance sample. Both satisfied laboratory test requirements of the specification. The surveillance sample showed the maximum allowable viscosity change of -5% in the accelerated stability test, but all other tests were well within requirements.

Superimposed spectra of a qualification and two surveillance samples of VV-L-800 preservative oil are shown in Figure 1C. The absorption band marked at 1060 cm^{-1} is characteristic of the calcium or barium sulfonate corrosion inhibitors. Both surveillance samples in this



**SUPERIMPOSED INFRARED SPECTRA OF FINISHED
PRESERVATIVE FORMULATIONS. QUALIFICATION
SAMPLES - q; SURVEILLANCE SAMPLES - s.**

**A. MIL-C-372 B. MIL-L-3150
C. VV-L-800**

FIGURE 1

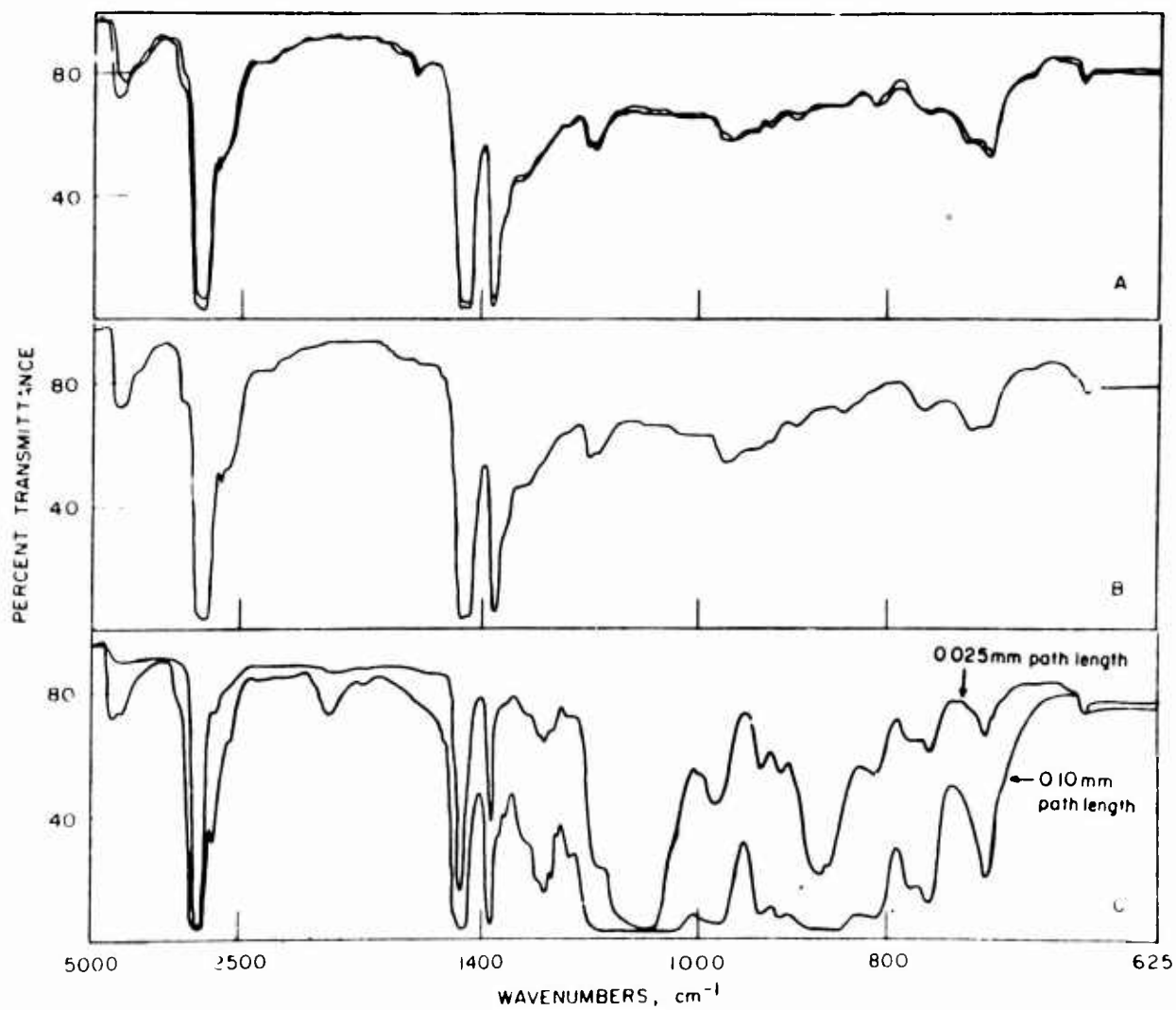
case failed the corrosivity test required by the specification. The differences in transmittance at 1060 cm^{-1} indicate that there were smaller amounts of sulfonate inhibitor in the surveillance samples than in the qualification sample.

Figure 2 shows spectra of three base oils. Two superimposed curves for the same oil sample in Figure 2A show the reproducibility of the spectra. Reproducibility of the various absorption points falls within the $\pm 2\%$ transmittance limits set by Crilly⁽³⁾. Figure 2C shows that, with the same 0.10 mm. path length used for the petroleum base oils, the silicate base oil gives much heavier absorption. With a shorter path length the spectrum of the silicate is better defined but the reproducibility, which is not shown here, is much less.

Curves shown in Figure 3 indicate that two additives, used here in concentrations near those typical of VV-L-800 formulations, are not detectable in the spectrum. Differences at the two ends of the spectrum are not significant. None of the absorption bands in the spectra of the additives appears in the spectra of the partial formulations shown in Figures 3B and D. It must also be remembered that a typical VV-L-800 formulation will contain several additives in addition to the single additive used in each of these partial formulations. Combinations of additives will further obscure or confuse absorption bands in a finished formulation.

Figure 4 shows spectra of two antioxidants alone and dissolved in a MIL-H-46004 base oil. At the concentration level used, the cadmium diamyldithiocarbamate did not appear in the spectrum of Figure 4B. Two absorption bands at 1370 and 1490 cm^{-1} , marked by the arrows in Figure 4A, are probably bands in the spectrum of the base oil vehicle for the antioxidant. The third band between these two is obscured by the base oil in the spectrum of the partial formulation in Figure 4B. Phenyl-alpha-naphthylamine, however, does appear in the spectrum of its partial formulation. The arrows in Figure 4D mark absorption bands which detect the latter compound.

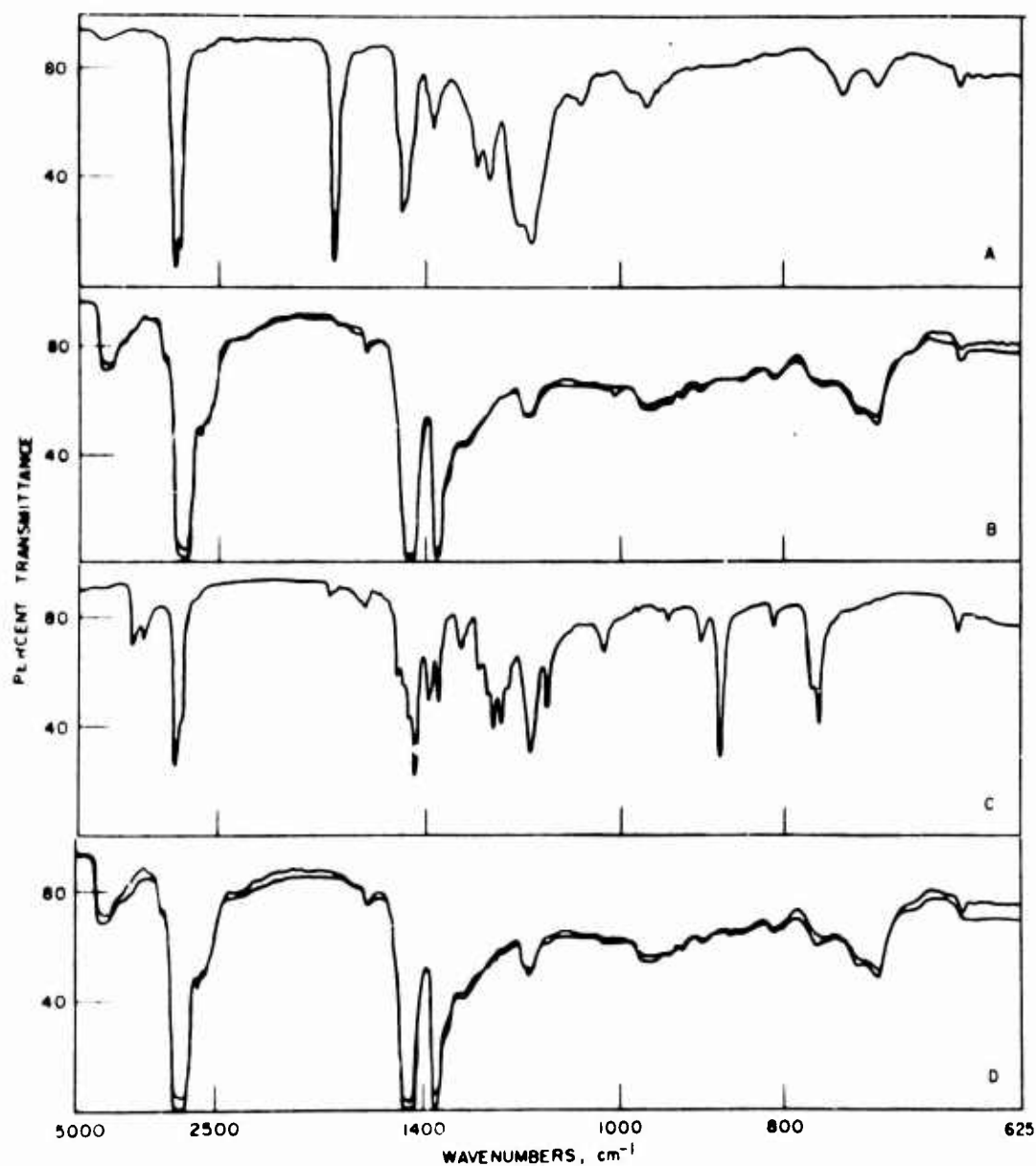
In Figure 5 are shown spectra of a calcium sulfonate and a barium dinonylnaphthalene sulfonate corrosion inhibitor alone and dissolved in base oil. It is evident that, at the concentrations used, these inhibitors are easy to detect, although they may be difficult to distinguish from one another in a formulation. The absorption bands between 1000 - 1100 cm^{-1} are deep enough to be used for quantitative determinations. Crilly and McGowan⁽⁴⁾ demonstrated that such a quantitative measurement



**SPECTRA OF BASE OILS
DUPLICATE SPECTRA SUPERIMPOSED**

**A. VV-L-800 B. MIL-H-46004
C. MIL-L-14107B**

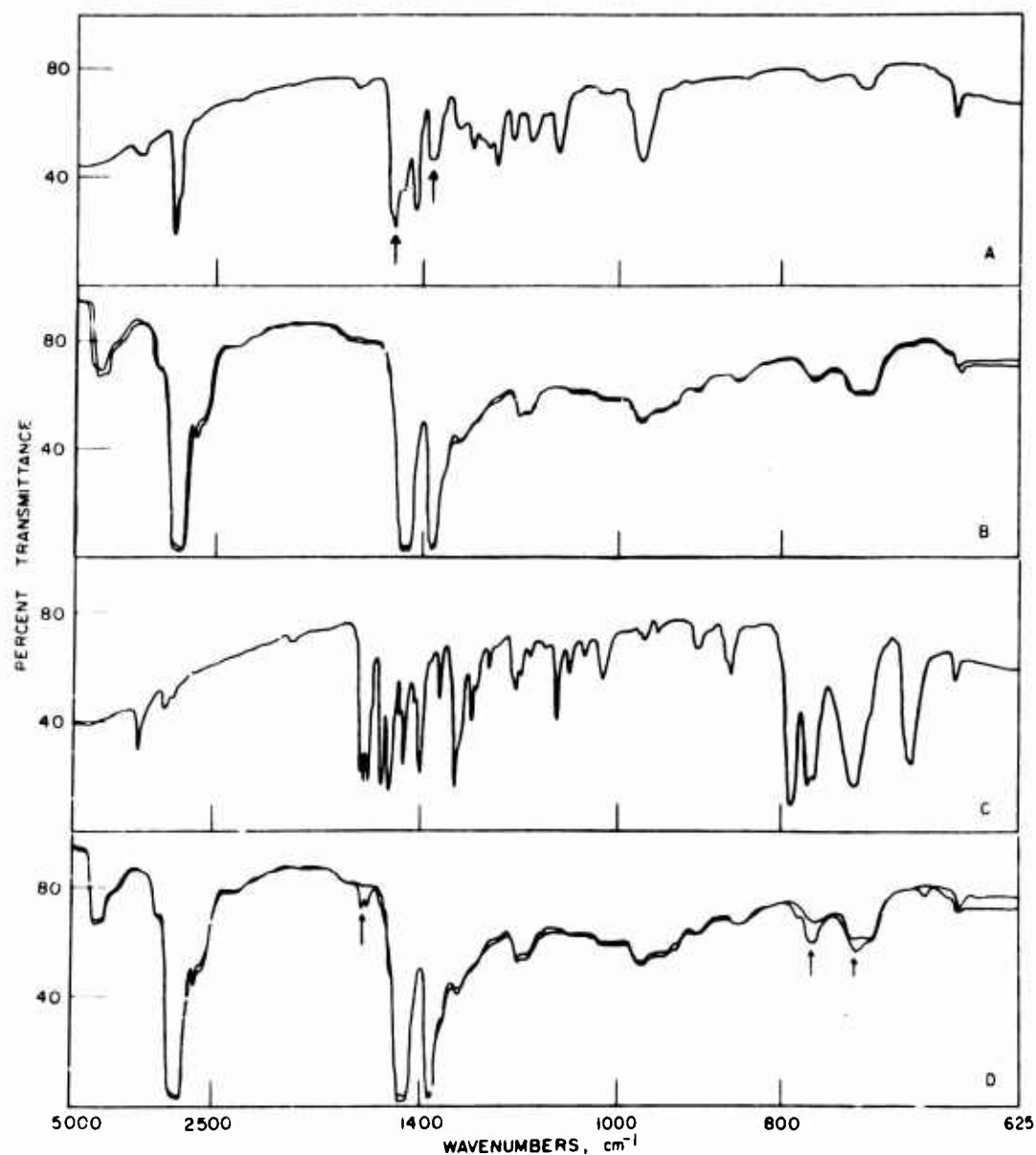
FIGURE 2



**SPECTRA OF ADDITIVES ALONE AND DISSOLVED
IN VV-L-800 BASE OIL**

- A. Poly acrylate.
- B. Superimposed spectra. Base oil and 0.3% by wt. poly acrylate in base oil.
- C. 2,6-di-tert-butyl-p-cresol.
- D. Superimposed spectra. Base oil and 0.6% by wt. 2,6-di-tert-butyl-p-cresol in base oil.

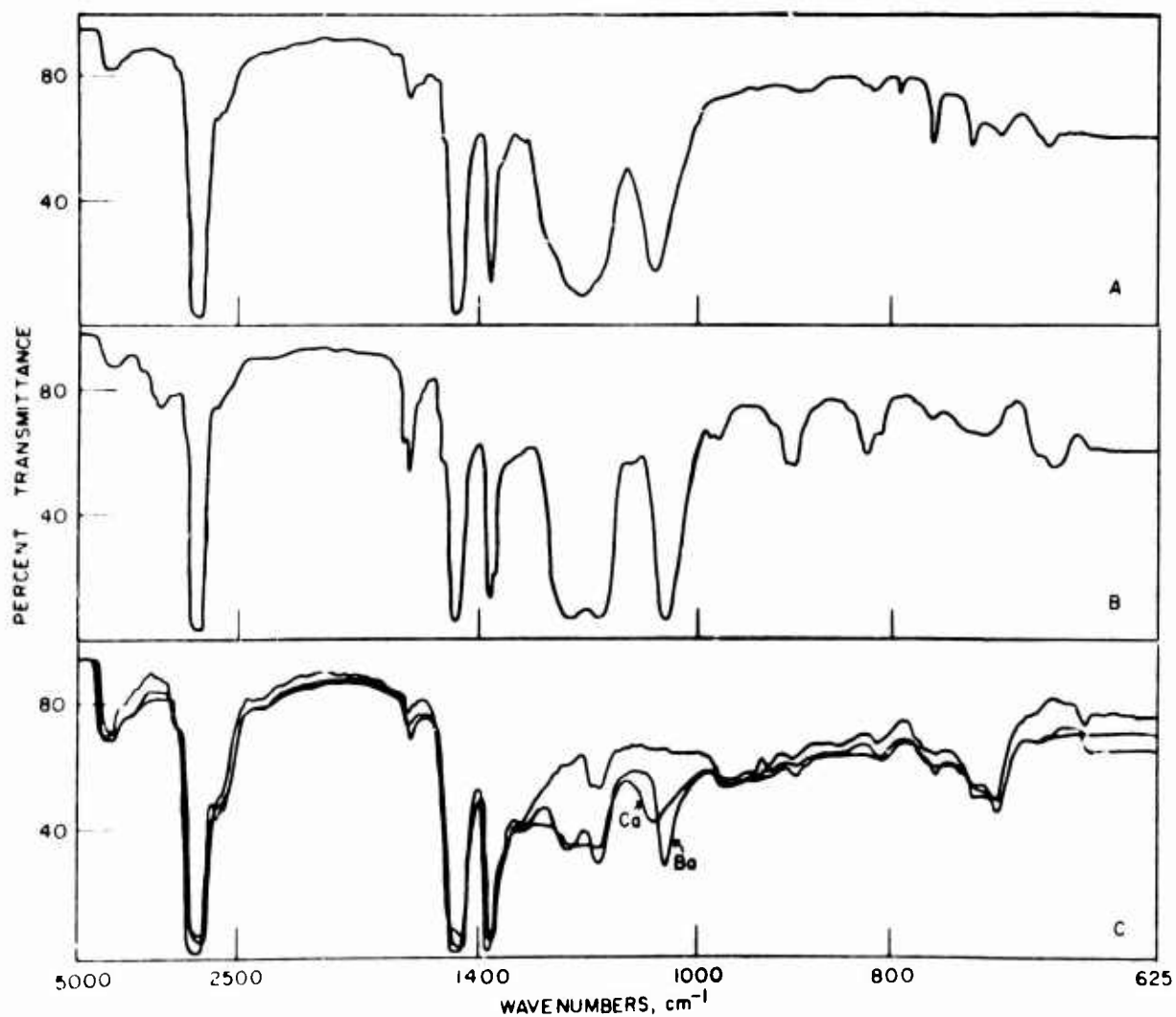
FIGURE 3



**SPECTRA OF ADDITIVE ALONE AND DISSOLVED
IN MIL-H-46004 BASE OIL**

- A. Cadmium diamyldithiocarbamate.
- B. Superimposed spectra. Base oil and 0.3% by wt. cadmium diamyldithiocarbamate in base oil.
- C. Phenyl-alpha-naphthylamine.
- D. Superimposed spectra. Base oil and 0.6% by wt. phenyl-alpha-naphthylamine in base oil.

FIGURE 4



**SPECTRA OF ADDITIVES ALONG AND DISSOLVED
IN VV-L-800 BASE OIL**

- A. Calcium petroleum sulfonate.**
- B. Barium dinonylnaphthalene sulfonate.**
- C. Superimposed spectra. Base oil, 4.6% by wt. barium sulfonate in base oil (Ba), and 4.4% by wt. calcium sulfonate in base oil (Ca).**

FIGURE 5

is possible.

Figure 6 shows the spectrum of tricresyl phosphate and superimposed spectra of solutions of 0, 0.21, 0.44, and 0.64% by weight tricresyl phosphate in a MIL-H-46004 base oil. The absorption band marked by the arrow can be used for quantitative analysis as will be shown later in this report.

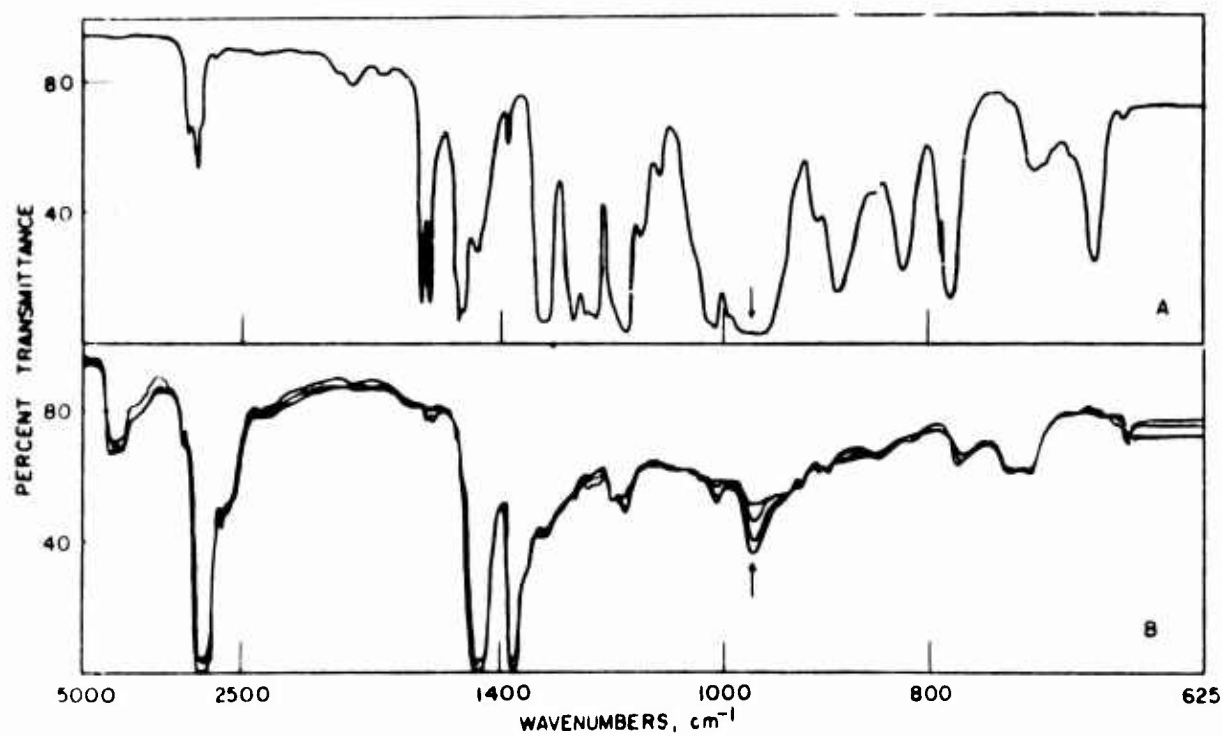
The heavy absorption of the MIL-L-14107 silicate base oil mentioned earlier in this report obscured the absorption bands of all additives tried in this oil. However, when a sample of the base oil was placed in a variable path length cell in the reference beam of the spectrophotometer, absorption bands were detected for the calcium and barium sulfonate inhibitors, dioctyldiphenylamine and phenyl-alpha-naphthylamine. Cadmium diamyl-dithiocarbamate probably showed absorption, but this was questionable. Its spectra should be checked further. Quinazarin was not detected. It has a solubility of less than 0.03% by weight in the oil. The dye is also used at a low concentration and was not detected.

A method for quantitative determination of additives is shown by the following. Figure 7 shows part of the spectrum of 0.9% by weight phenyl-alpha-naphthylamine in silicate base oil with a sample of the base oil placed in the reference beam. The spectrum of this additive is similar when it is placed in the MIL-H-46004 oil. Background transmittance is marked by the point T_b ; T_p is transmittance of the absorption peak. Absorbance, A , is defined by

$$A = \log_{10} \frac{T_b}{T_p} \quad [1]$$

For the transmittance values shown in Figure 7, A is $\log 77.5/66.5$ or 0.066.

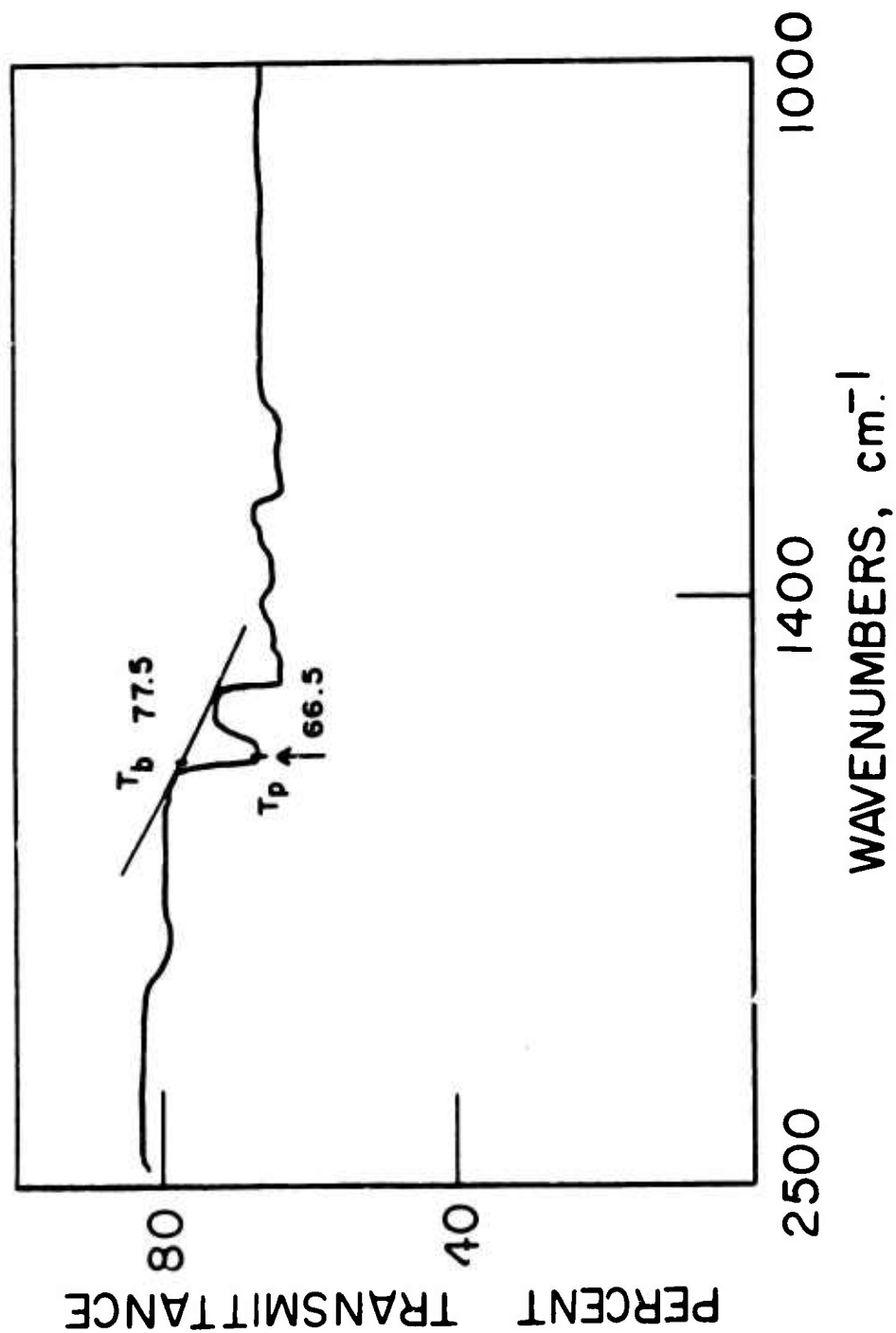
Figure 8 shows concentration vs. absorbance curves for two additives in MIL-H-46004 base oil. The figure shows that these materials follow Beer's law over the concentration range used. Crilly and McGowan⁽⁴⁾ showed that the sulfonates also follow Beer's law in petroleum base oils. It appears reasonable to assume that the remaining materials investigated here also show linear concentration-absorbance relationships because of the small and low concentration range used. These facts and assumption are used here to arrange the additives studied in order of their detection limits.



**SPECTRA OF ADDITIVES ALONE AND DISSOLVED
IN MIL-H-46004 BASE OIL**

- A. Tricresyl phosphate.**
- B. Superimposed spectra. Base oil and solutions of 0.21, 0.44 and 0.64% by wt. tricresyl phosphate.**

FIGURE 6



PORTION OF THE SPECTRUM OF PHENYL-ALPHA-NAPHTHYLAMINE
CONCENTRATION 0.9% BY WT. IN MIL-L-14107 BASE OIL.
SPECTRUM COMPENSATED BY BASE OIL IN REFERENCE BEAM.

FIGURE 7

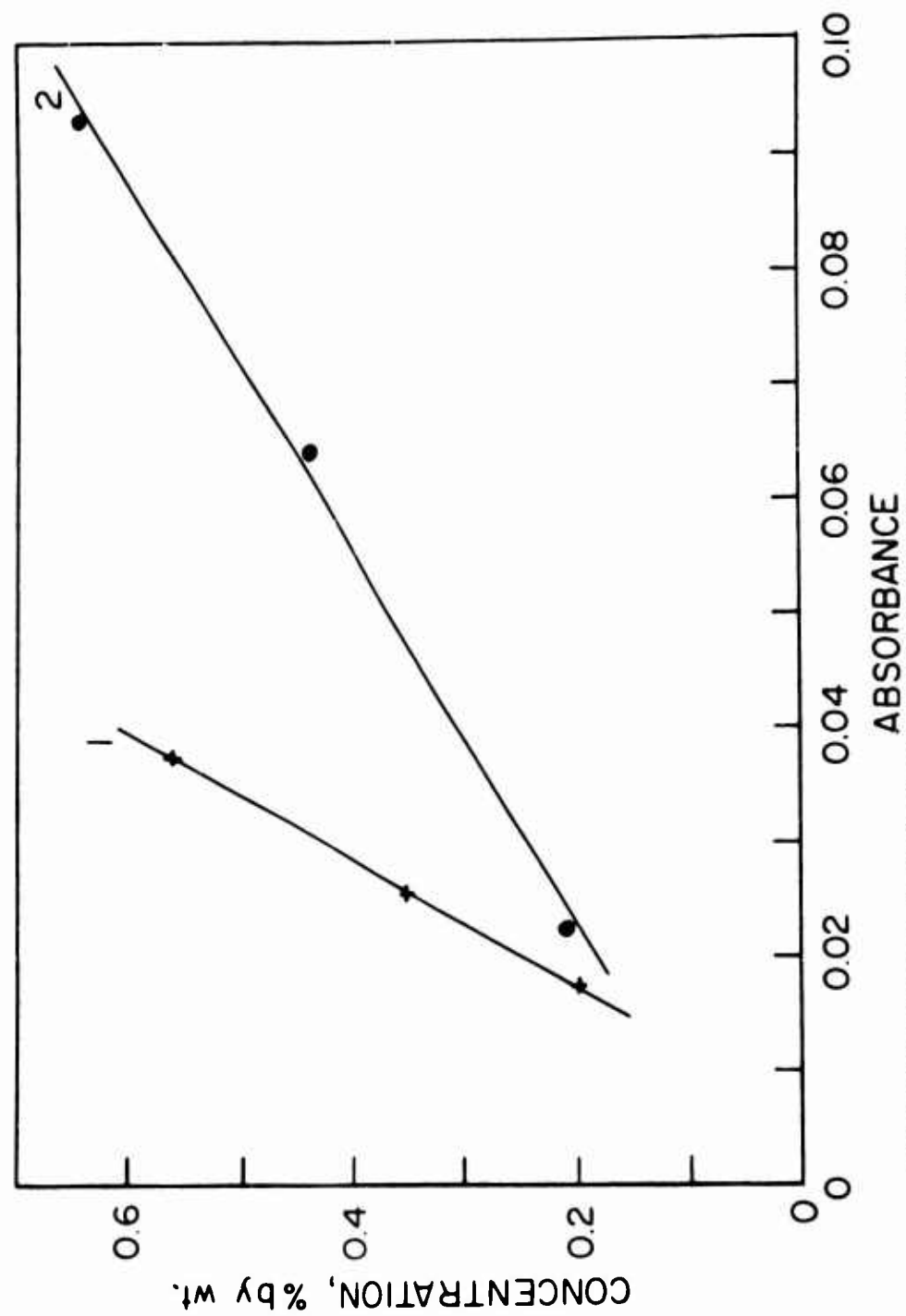


FIGURE 8

The $\pm 2\%$ transmittance tolerance limits mentioned earlier in this report form the basis for an arrangement of the additives in order of detection limits. If the background transmittance can be reproduced to $\pm 2\%$ and the peak transmittance can also be reproduced to $\pm 2\%$, then the maximum differences expected in an absorption band would be 4%. Any material which absorbed less than 4% was taken to be not detectable. The absorbance corresponding to a 4% transmittance change was found at a suitable frequency for each additive solution in its base oil. Its limit of detection was then estimated assuming Beer's law held from the absorbance at the actual concentration used down to the absorbance for a 4% transmittance change. Table I shows results of this estimation. The table shows that use of base oil in the reference beam improves the ability of the spectra to show the presence of additives in the silicate base oil. Little improvement is apparent in the base oils derived from petroleum. The actual values of concentrations shown may vary somewhat, depending on the instrument used, the method of obtaining spectra, and possible variations from the $\pm 2\%$ limits taken as the basis for this comparison.

Results of this study indicate, in general, that for the base oils derived from petroleum the sulfonates and tricresyl phosphate are readily detected by infrared spectra. Minor ingredients in formulations such as anti-oxidants are used in concentrations which are near or below their detection limits. In the silicate base oil none of the additives studied could be detected in the simple spectrogram.

Some method of concentration of additives appears to be necessary in order to improve the infrared spectrographic method for detection of changes or variations in formulation. The concentrations generally need to be increased by no more than a factor of two or three times to make the method much more useful. A chromatographic method using columns of activated alumina, silica and fuller's earth to adsorb the polar additives seems applicable.

One difficulty encountered in making any meaningful correlation between spectra and laboratory test results is caused by the time span between receipt of the qualification sample and receipt and testing of the surveillance sample. For example, for the MIL-C-372, MIL-L-3150, and VV-L-800 samples shown in Figure 1, the times between reports on the qualification and surveillance samples were four, four and three years, respectively. In view of the wide variations in spectra shown by the

TABLE I

DETECTION LIMITS OF SOME ADDITIVES
SPECTRA COMPENSATED AND UNCOMPENSATED BY BASE OIL IN REFERENCE BEAM

Additive	Approx. Min. Conc. Detectable, % by wt.	
	<u>Compensated</u>	<u>Uncompensated</u>
In VV-L-800 and MIL-H-46004 base oils:		
Tricresyl phosphate	0.1	0.1
p,p'-Dityldiphenylamine	0.3	-
Phenyl-alpha-naphthylamine	0.3	0.3
2,6-di-tert-Butyl-p-cresol	0.4	>0.6(a)
Nonylphenoxyacetic acid	0.4	0.4
Oleyl-linoleoyl sarcosines	0.6	0.7
Barium dinonylnaphthalene sulfonate	0.7	0.5
Calcium petroleum sulfonate	1.3	1.2
Cadmium diamyldithiocarbamate	>0.3(a)	>0.3(a)
Poly acrylate	>0.3(a)	>0.3(a)
"Oil Yellow N"	Conc. 100 ppm.	not detected
In MIL-L-14107 base oil:		
Phenyl-alpha-naphthylamine	0.3	>1.5(a)
p,p'-Dioctyldiphenylamine	0.3	>0.9(a)
Calcium petroleum sulfonate	0.6-0.8	>4.9(a)
Cadmium diamyldithiocarbamate	>1.0(a)	>1.0(a)
Quinazolin	Solubility	<0.03% not detected

(a) Highest concentration used.

three MIL-C-372 samples, all of which met specification requirements, it is questionable whether a meaningful correlation can be established in any reasonable time between spectra and laboratory tests for this specification. Infrared spectra are already useful, however, for diagnostic tests as illustrated in Figure 1C.

Infrared spectra should be used cautiously as an inspection tool in specification testing. This is not to say that when a change in the spectrum greater than some accepted tolerance limit is observed, there has been no change in the formulation. The point is that some additives can be omitted, replaced, or changed in concentration without these changes being detected in the spectrum obtained without compensation for the base material. This will be true as long as a composition requirement is not included in the specification, or until some separation method is used prior to obtaining the spectrogram.

CONCLUSIONS AND RECOMMENDATIONS

For the types of formulations studied here, the simple infrared spectrum cannot accurately detect changes or variations in formulation. Even when the composition is known, some additives escape detection. A sample of a formulation's base oil placed in the reference beam improves the limit of detection of additives.

It is recommended that the next phase of work on this problem include use of chromatographic methods for concentration and separation of additives.

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13 ABSTRACT An effort was made to ascertain whether infrared spectro- graphic analysis could detect changes in composition of formulations of preservative, hydraulic and specialty fluids covered by specifi- cations for which Rock Island Arsenal has qualification responsi- bility. Limits of detection of additives were estimated using both spectra compensated by base oil in the reference beam of the spectro- photometer and simple, or uncompensated spectra. Petroleum type base oils for VV-L-800 and MIL-H-46004 and a tetra-alkyl silicate base fluid for MIL-L-14107 were used. Additives studied were several corrosion inhibitors, antioxidants, antiwear agent, a hydrolysis inhibitor, a pour point depressant and a dye. It was found that the heavy absorption of the silicate base oil obscured absorption bands of all additives tested in it. In the petroleum base oils the corrosion inhibitors and tricresyl phosphate were easily detected. The remaining additives are used near or below their detection limits. Use of the formulation's base oil in the reference beam improved the limit of detection of additives. It was concluded that the infrared spectrogram cannot accurately detect changes in formulation. The recommendation is made that methods for concentration of additives be used before obtaining the infrared spectrogram in order to improve on their detection. (U) (Author)		

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	<p>Corrosion Preventive Hydraulic Fluid Specialty Fluids Infrared Spectrogram Identification</p>						

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three MIL-C-372 samples, all of which met specification requirements, it is questionable whether a meaningful correlation can be established in any reasonable time between spectra and laboratory tests for this specification. Infrared spectra are already useful, however, for diagnostic tests as illustrated in Figure 1C.

Infrared spectra should be used cautiously as an inspection tool in specification testing. This is not to say that when a change in the spectrum greater than some accepted tolerance limit is observed, there has been no change in the formulation. The point is that some additives can be omitted, replaced, or changed in concentration without these changes being detected in the spectrum obtained without compensation for the base material. This will be true as long as a composition requirement is not included in the specification, or until some separation method is used prior to obtaining the spectrogram.

CONCLUSIONS AND RECOMMENDATIONS

For the types of formulations studied here, the simple infrared spectrum cannot accurately detect changes or variations in formulation. Even when the composition is known, some additives escape detection. A sample of a formulation's base oil placed in the reference beam improves the limit of detection of additives.

It is recommended that the next phase of work on this problem include use of chromatographic methods for concentration and separation of additives.